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(54) Title of the Invention: **Polyester Resin Composition**

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SPECIFICATION

1. Title of the Invention

Polyester Resin Composition

2. Claims

A polyester resin composition formed as a result of adding 0.005 to 10 parts by weight of a β -diketone with a molecular weight of 150 or more having the structural units of general formula (I), and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.



(In the formula, R is a hydrogen atom, alkyl group, or aromatic group.)

3. Detailed Description of the Invention

(Field of Industrial Utilization)

The present invention relates to a polyester resin composition in which the crystallization velocity is high, the mold release characteristics of a molded article are excellent when a low-temperature mold is used, gas generation is minimal, and the reduction in molecular weight is low during molding and manufacturing of the resin composition.

(Prior Art)

Thermoplastic polyester resins are widely used in a broad range of fields such as fibers, films, and bottles on the basis of their superior mechanical properties and physicochemical characteristics. Among these resins, polybutylene terephthalate and other polyesters with a high crystallization velocity are used in large quantities in injection molding, but from the aspect of reducing manufacturing costs and the like, there is a demand for higher crystallization velocity. Polyethylene terephthalate is a typical example of the polyesters that are currently underutilized in injection molding applications, and the reason for this is that since the crystallization velocity of such polyesters is low, there are drawbacks in that the molding cycle is prolonged and the mold must be set to a high temperature.

In order to resolve such difficulties, methods have been proposed whereby talc and other inorganic material; the higher fatty acid salts disclosed in JP (Kokai) Nos. 55-52340, 55-60552, and other publications; the acetylacetone metal salts disclosed in JP (Kokai) Nos. 56-41247, 57-14644, and other publications; the alkaline metal salts of dehydroacetic acid disclosed in JP (Kokai) 63-15840; and other substances are added as crystallinity improvers.

(Problems to Be Solved by the Invention)

However, the crystallization velocity of polyester is not significantly improved as a result of these methods, and they present additional drawbacks in that large quantities of gas are produced during molding, and the mechanical characteristics also tend to be compromised.

(Means Used to Solve the Above-Mentioned Problems)

In view of the above, the present inventors, as a result of thoroughgoing research aimed at obtaining a crystallinity improver in which the crystallization of polyester is markedly improved and the generation of gas during molding is low, arrived at the present invention

having discovered that the initial problems can be solved when a β -diketone having a specific structure and molecular weight, and/or a metal chelate thereof, is added to polyester, and that the compounds are very effective in preventing a reduction in molecular weight during the manufacture of polyester resin compositions in which the crystallization velocity is improved, which has conventionally been difficult.

More specifically, the present invention provides a polyester resin composition formed as a result of adding 0.005 to 10 parts by weight of a β -diketone with a molecular weight of 150 or more having the structural units of general formula (I), and/or a metal chelate thereof, per 100 parts by weight of thermoplastic polyester.



(In the formula, R is a hydrogen atom, alkyl group, or aromatic group.)

The thermoplastic polyester used in the present invention is a polymer or copolymer obtained as a result of a polycondensation reaction in which the main components are a dicarboxylic acid (or an ester-forming derivative thereof) and a diol (or an ester-forming derivative thereof).

Examples of the dicarboxylic acid used herein include terephthalic acid, isophthalic acid, orthophthalic acid, 1,5-naphthalene dicarboxylic acid, 2,5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 2,2'-biphenyl dicarboxylic acid, 3,3'-biphenyl dicarboxylic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-biphenylether dicarboxylic acid, 4,4'-diphenylmethane dicarboxylic acid, 4,4'-diphenylsulfone dicarboxylic acid, 4,4'-diphenyl isopropylidene dicarboxylic acid, 1,2-bis(phenoxy) ethane-4',4''-dicarboxylic acid, 2,5-anthracene dicarboxylic acid, 2,6-anthracene dicarboxylic acid, 4,4'-p-terphenylene dicarboxylic acid, and 2,5-pyridine dicarboxylic acid; and preferable among these is terephthalic acid.

Two or more of these dicarboxylic acids may be mixed and used together. It should be noted that in addition to these dicarboxylic acids, one or more of the following may be mixed and used in small amounts: aliphatic dicarboxylic acids such as adipic acid, azelaic acid, dodecanedioic acid and sebacic acid; and cycloaliphatic dicarboxylic acids such as cyclohexane dicarboxylic acid.

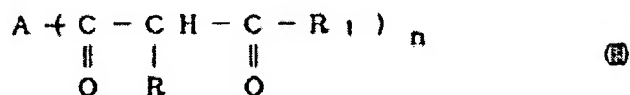
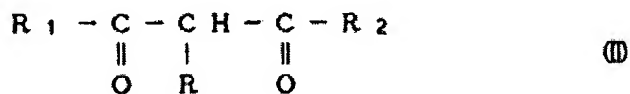
Examples of the diol component include ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol, 2-methyl-1,3-propane diol, diethylene glycol,

triethylene glycol, and other aliphatic diols; 1,4-cyclohexane dimethanol, and other cyclo-aliphatic diols; and mixtures thereof. One or more of the following with a molecular weight of 400 to 6,000 may be copolymerized as long as they are used in a small amount: polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and other long-chain diols.

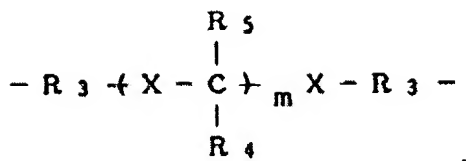
Specific examples of the polyester include polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, polybutylene naphthalate, and polyethylene-1,2-bis(phenoxy) ethane-4',4"-dicarboxylate, as well as copolyesters such as polyethylene isophthalate/terephthalate, polybutylene terephthalate/isophthalate, and polybutylene terephthalate/decane dicarboxylate. Preferred among these are polybutylene terephthalate, polycyclohexane dimethylene terephthalate, polyethylene naphthalate, and polyethylene terephthalate, which have a good balance between mechanical properties and moldability.

The polyester used in the present invention has an intrinsic viscosity of 0.25 to 3.0 dL/g, and preferably 0.4 to 2.25 dL/g, when measured at a temperature of 25°C in an o-chlorophenol solution.

The β -diketones used in the present invention are not particularly limited as long as they have the structural units of the general formula (I) and a molecular weight of 150 or more, but particularly preferred are those with the structures of the following general formulas (II) and (III).



(In the formulas, R_1 and R_2 are alkyl groups, aromatic groups, or aliphatic-alicyclic groups. R and R_1 , or R_1 and R_2 may bond together to form a ring structure. The symbol n represents a number 2 to 4. A is a direct bond, a hydrocarbon group with a valence of 2 to 4,



or



As used herein, R₃ is an alkylene group; R₄ and R₅ are each a hydrogen atom, alkyl group, or aromatic group; R₄ and R₅ may bond together to form a ring structure; X represents -O- or -S-; the symbol m is 0 to 1; and R₆ is a hydrogen atom, an alkyl group, an aromatic group, or R₃.)

It should be noted that the chemical structure of the β -diketones is always referred to in the present invention as a keto structure, but the structure may also be a compound described as a corresponding ethanol structure. Also, as long the structure has the structural units of formula (I), it may be a compound having a ketone group, that is, a triketone, tetraketone, or another ketone compound.

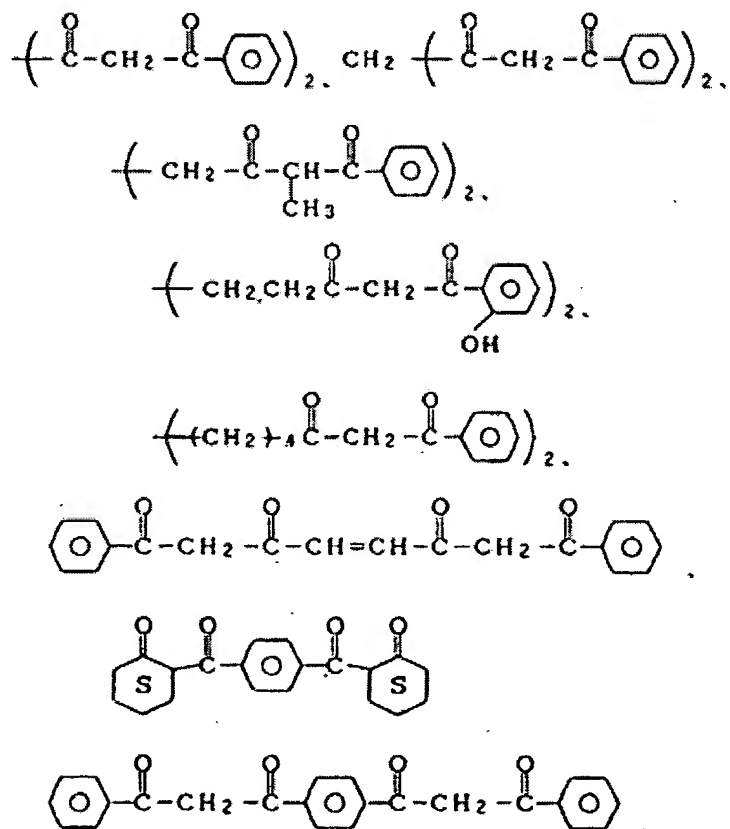
Specific examples of R, R₁, R₂, R₄, R₅, and R₆ include methyl, ethyl, propyl, butyl, hexyl, octadecyl, benzyl, cyclohexyl, and other alkyl groups; and phenyl, naphthyl, methylphenyl, chlorophenyl, hydroxyphenyl, and other aromatic groups. Examples of groups when R and R₁, R₁ and R₂, or R₄ and R₅ bond to form a ring structure include trimethylene, tetramethylene, and pentamethylene. R₃ may be methylene, ethylene, propylene, or another alkylene group. Examples of A as a hydrocarbon group with a valence of 2 to 4 include methylene, ethylene, propylene, cyclohexylene, vinylene, phenylene, butanetriyl, benzenetriyl, and ethylenetetrayl. Of the compounds shown with the help of the general formula (I), one that has at least one unsaturated bond in the molecule is preferred, and preferably has an aromatic group. More preferable is one that has an unsaturated bond that conjugates with at least one carbonyl carbon of a β -diketone, and preferably has an aromatic group. Also, R is more preferably a hydrogen atom.

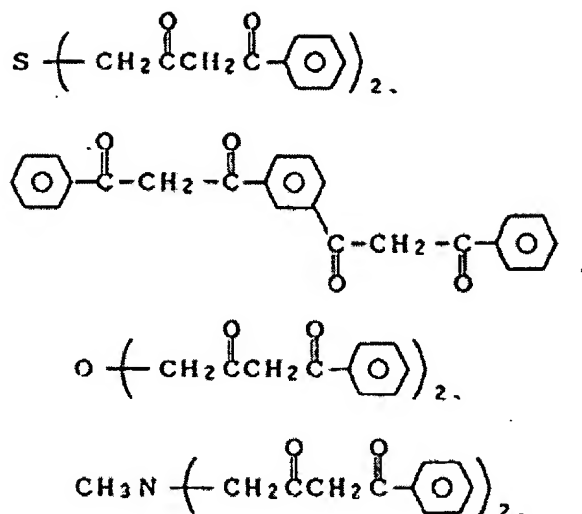
Specific examples of the compounds shown with the help of the general formula (I) include 2,4-octadecanediol, benzoyl acetone, benzoyl trifluoroacetone, dibenzoyl methane, furoyl acetone, benzoyl furoyl methane, thenoyl acetone, furoyl thenoyl methane, 2'-hydroxybenzoyl acetone, 2'-hydroxybenzoyl-benzoyl methane, bis-2'-hydroxybenzoyl methane,

1,1-dibenzoyl hexane, 1,1-dibenzoyl octadecane, dicyclohexane carbonyl methane, dinaphthoyl methane, and dicinnamoyl methane. Preferred examples include benzoyl acetone, benzoyl trifluoroacetone, dibenzoyl methane, furoyl acetone, benzoyl furoyl methane, thenoyl acetone, furoyl thenoyl methane, 2'-hydroxybenzoyl acetone, 2'-hydroxybenzoyl-benzoyl methane, bis-2'-hydroxybenzoyl methane, 1,1-dibenzoyl hexane, 1,1-dibenzoyl octadecane, dinaphthoyl methane, and dicinnamoyl methane. Among these in particular, the most preferred examples include dibenzoyl methane, 2'-hydroxybenzoyl acetone, bis-2'-hydroxybenzoyl methane, dinaphthoyl methane, and dicinnamoyl methane.

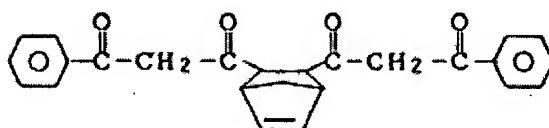
Of the compounds shown with the help of the general formula (III), at least R_1 or A is preferably an unsaturated bond that conjugates with the carbonyl carbon of a β -diketone, and is preferably an aromatic group. Both R_1 and A are preferably unsaturated bonds that conjugate with carbonyl carbon, and preferably are aromatic groups.

Examples of the compounds expressed with the help of the general formula (III) include those shown below:





and



The molecular weight of the β -diketones of the present invention must be 150 or more, is more preferably 175 or more, and is most preferably 200 or more. If the molecular weight is less than 150, not only is the amount of gas generated during molding high, but also the crystallinity is poor and there is considerable reduction in molecular weight of the polyester during the manufacture of the resin composition, and such a molecular weight is not preferred.

In the case of the β -diketones expressed with the help of the general formula (I) of the present invention, R must be a hydrogen atom, an alkyl group, or an aromatic group, and among these a hydrogen atom is preferred.

Other than these substituents, when R has a substituent such as an acyl group, alkyloxy group, amino group, or hydroxyl group, for example, the crystallinity of the polyester resin composition is poor, and the molecular weight of the polyester is considerably reduced during the manufacture of the resin composition.

Even if the compound has the structure of general formula (I) in the molecule and has a molecular weight of 150 or more, the molecular weight of the polyester still decreases considerably during the manufacture of the resin composition even in the case in which a compound other than a β -diketone, such as a β -ketoester, a malonic acid ester derivative, and/or

metal chelate thereof, is added to the thermoplastic polyester, and such an addition is therefore not preferred.

Examples of the metals in the metal chelates of the β -diketones of the present invention include lithium, sodium, potassium, cesium, rubidium, and other alkali metals; barium, strontium, calcium, magnesium, and other alkaline-earth metals; and titanium, iron, and the like. Among these, sodium, potassium, and lithium are preferred.

In the present invention, the β -diketone and/or metal chelate thereof may be used alone, or two or more types may be used together.

The addition amount of the β -diketone having the structural units of general formula (I) and a molecular weight of 150 or more according to the present invention, and/or metal chelate thereof, is 0.005 to 10 parts by weight, is preferably 0.01 to 5 parts by weight, and is more preferably 0.05 to 5 parts by weight, per 100 parts by weight of the thermoplastic polyester. If the addition amount is less than 0.005 parts by weight, the effect of improving the crystallinity of the polyester is not sufficient, and if the addition amount exceeds 10 parts by weight, the molecular weight of the polyester during manufacture of the polyester resin composition decreases, and the dynamic properties of the molded article tend to be compromised, and both cases are accordingly not preferred.

From the viewpoint of improving moldability, the composition of the present invention is preferably jointly used as required with organic acid salts or inorganic compounds. Specific examples of such compounds include sodium stearate, barium stearate, sodium salts or barium salts of partially saponified montanic acid esters, ionomers, sodium salts of phenols such as nitrophenol and formyl phenol, and talc.

Furthermore, the moldability can be further improved with the help of a method in which a compound known as a crystallization promoter and used in thermoplastic polyesters such as polyethylene terephthalate is added to the composition of the present invention. Specific examples of such crystallization promoters include polyethylene glycol, polypropylene glycol, and other polyalkylene glycols or carboxylic acid diesters thereof; α,ω -dialkyl etherified polyethylene glycols, α,ω -dialkyl etherified polypropylene glycols, and other α,ω -dialkyl etherified polypropylene glycols; neopentyl glycol dibenzoate and other benzoic acid ester compounds; and polylactone, polyethylene adipate, and other aliphatic polyesters.

It should be noted that as a result of further adding fibrous and/or granular fillers to the composition of the present invention, the rigidity can be considerably improved without compromising other physical properties, although this is not essential. Examples of such fillers include glass fibers, carbon fibers, metal fibers, aramid fibers, asbestos, potassium titanate whiskers, wollastonite, glass flakes, glass beads, talc, mica, clay, calcium carbonate, barium sulfate, titanium oxide, and aluminum oxide. Preferably used among these are chopped strand types of glass fiber, talc, and titanium oxide. The amount of the fillers added is ordinarily equal to or less than 120 parts by weight per 100 parts by weight of the polyesters.

One or more of ordinary additives such as antioxidants, thermostabilizers, UV absorbers, lubricants, mold release agents, and colorants, including dyes and pigments, may be added to the composition of the present invention in a range that does not compromise the object of the present invention.

A small amount of thermoplastic resin (examples of which include polycarbonate, polyphenylene ether, polyamide, polypropylene, polyethylene, ionomer, ethylene/propylene copolymer, ethylene/butene-1 copolymer, ethylene/propylene/non-conjugated diene copolymer, ethylene/ethyl acrylate copolymer, ethylene/glycidyl methacrylate copolymer, ethylene/vinyl acetate/glycidyl methacrylate copolymer, and ethylene/propylene-g-maleic anhydride copolymer) may also be added.

The method of producing the composition of the present invention is not particularly limited, but examples of preferably used methods include a method in which both a polyester and a β -diketone, and/or a metal chelate thereof, are melted and mixed using an extruder, and a method for adding a β -diketone compound or a metal chelate thereof in the final stage of polymerization of the polyester. When inorganic filler or another additive is added, the additive is preferably melted and blended in at the same time as the two components described above using an extruder.

The resin composition of the present invention can easily be molded by means of injection molding, extrusion molding, or another ordinary method, and the resulting molded article has high crystallinity and exhibits excellent properties.

Working Examples

The effect of the present invention is described in greater detail with working examples below.

The intrinsic viscosities in the examples are values measured in an o-chlorophenol solution at 25°C, and the parts and percentages are both based on weight.

Working Examples 1 to 4 and Comparative Examples 1 to 7

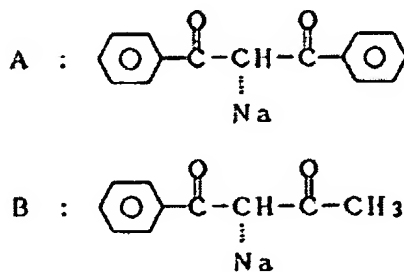
Additives (A) to (F) described below were blended in the ratios shown in Table 1 based on 100 parts by weight of polyethylene terephthalate (PET) with an intrinsic viscosity of 0.83 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

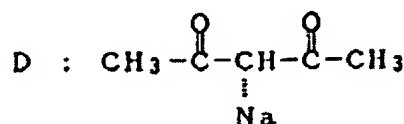
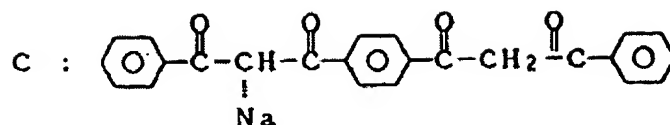
The resulting polyethylene terephthalate composition was subjected to differential thermal analysis using a differential scanning calorimeter manufactured by PerkinElmer Inc., and the heating crystallization temperature and cooling crystallization temperature were measured and crystallinity was evaluated. It is generally well known that crystallinity is improved as the cooling crystallization temperature increases and as the heating crystallization temperature decreases, so ΔT (defined as $\Delta T = (\text{Cooling crystallization temperature}) - (\text{Heating crystallization temperature})$) was therefore used as a measure for the crystallinity.

Next, the intrinsic viscosity of the resulting pellets was measured, and the result was used as a measure of the reduction in molecular weight of the polyester during the manufacture of the resin composition. Also, weight reduction was measured using a differential thermogravimeter when the pellets were left standing for one hour at a temperature of 290°C in nitrogen, and the result was used as a measure of the amount of gas released during molding.

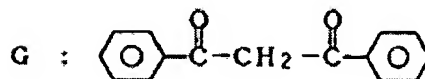
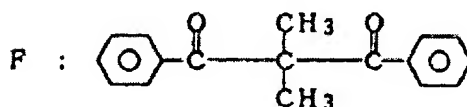
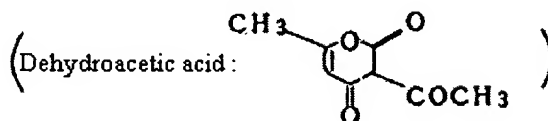
The results of the above are shown in Table 1.

(Additives)





E : Sodium salt of dehydroacetic acid



It is apparent from the results of Table 1 that the composition of the present invention is formed such that ΔT is considerable, the crystallization characteristics are markedly improved, the generation of gas is minimal, and the reduction in molecular weight is low during composition production.

Working Example 5 and Comparative Example 6

Additive (G) was blended in the ratio shown in Table 1 based on 100 parts by weight of polybutylene terephthalate (PBT) with an intrinsic viscosity of 0.74 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 260°C.

Next, the intrinsic viscosity of the resulting pellets was measured, and the result was used as a measure of the reduction in molecular weight of the polyester during the manufacture of the resin composition. Also, weight reduction was measured using a differential thermogravimeter when the pellets were left standing for one hour at a temperature of 270°C in nitrogen, and the result was used as a measure of the amount of gas released during molding. The example (comparative example 6) in which the additive (G) was not added was measured in the same manner at the same time.

The results of the above are shown in Table 1.

Working Example 6 and Comparative Example 7

Additive (A) was blended in the ratio shown in Table 1 based on 100 parts by weight of polycyclohexane dimethylene terephthalate (PCT) with an intrinsic viscosity of 0.94 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 305°C.

Next, the intrinsic viscosity of the resulting pellets was measured, and the result was used as a measure of the reduction in the molecular weight of the polyester during the manufacture of the resin composition. Also, weight reduction was measured using a differential thermogravimeter when the pellets were left standing for one hour at a temperature of 310°C in nitrogen, and the result was used as a measure of the amount of gas released during molding. The example (comparative example 6) in which the additive (G) was not added was measured in the same manner at the same time.

The results are shown in Table 1.

Working Examples 7 to 9 and Comparative Examples 8 to 11

Nucleating agents (A) to (F), and 50 parts of chopped-strand glass fiber (length: 3 mm, diameter: 11 μ) were blended in the ratios shown in Table 2 based on 100 parts by weight of polyethylene terephthalate with an intrinsic viscosity of 0.61 dL/g, and melt-blended into pellets using a twin-screw extruder with a diameter of 30 mm set to a temperature of 280°C.

The resulting polyethylene terephthalate composition was subjected to differential calorimetry and differential gravimetry in the same manner as described in working example 1.

The polyethylene terephthalate resin composition obtained by means of melt-kneading to form pellets was dissolved in o-chlorophenol, the glass fibers were separated using a centrifugal separator, and the solution was thereafter poured into methanol to obtain a polymer not containing glass fibers. The intrinsic viscosity of the resulting polymer was measured and used as the measure of molecular weight reduction during production of the resin composition in the presence of glass fibers.

The pellets were dried at 155°C for 5 hours in a vacuum, and boxlike molded articles were thereafter molded with a length of 45 mm, a width of 65 mm, a depth of 20 mm, and a wall thickness of 2 mm as a result of using a screw inline-type injection molding machine set to a temperature of 275°C, a mold clamping pressure of 75 tons, an injection time of 15 seconds, a

cooling time of 20 seconds, an intermediate time of 5 seconds, and a mold temperature of 90°C. The force (mold release force) required to release the molded article from the mold was then determined.

Table 1

Example		Nucleating agent		ΔT (°C) *1	Intrinsic viscosity (g/dL) ¹	Weight decrease (%) *2	Base polymer
		Type	Weight (parts)				
Working Example	1	A	0.5	86	0.79	0.92	PET
	2	A	2.0	92	0.72	1.2	PET
	3	B	0.5	82	0.76	1.0	PET
	4	C	0.5	83	0.77	0.89	PET
	5	G	2.0	163	0.72	0.65	PBT
	6	A	0.5	91	0.88	1.4	PCT
Comparative Examples	1	-	-	62	0.80	0.79	PET
	2	A	0.001	63	0.79	0.83	PET
	3	D	0.5	73	0.62	2.6	PET
	4	E	0.5	79	0.59	3.2	PET
	5	F	0.5	63	0.76	2.9	PET
	6	-	-	137	0.73	0.63	PBT
	7	-	-	69	0.92	1.3	PCT

*1: The quality of the crystals improves as the value of ΔT increases.

*2: The generation of gas is lower as the value of the weight reduction decreases.

Under the same injection molding conditions as described above, an ASTM-No. 1 dumbbell was molded, and the tensile strength and elongation at break were measured in accordance with ASTM D-638.

The results of the above are shown in Table 2.

¹ Should probably read (dL/g)

It is apparent from the results of Table 2 that the composition of the present invention considerably improves the crystallization characteristics even when glass fibers are present, and exhibits excellent mold release characteristics even in a low-temperature mold.

It is furthermore apparent that the generation of gas is minimal and the reduction in molecular weight is low when the composition is manufactured.

Table 2

Example		Nucleating agent		ΔT (°C) *1	Intrinsic viscosity (g/dL) ²	Weight decrease (%) *2	Mold release force kg f	Tensile strength (kg f/cm ²)	Breaking elongation (%)
		Type	Weight (parts)						
Working Examples	7	A	0.5	96	0.57	0.77	55	1,450	4.2
	8	B	0.5	92	0.55	0.89	40	1,500	3.9
	9	C	0.5	93	0.58	0.76	65	1,425	4.1
Comparative Examples	8	-	-	~50	0.58	0.78	> 200	1,225	3.4
	9	D	0.5	82	0.47	2.5	175	1,300	3.1
	10	E	0.5	79	0.42	2.9	120	1,275	2.9
	11	F	0.5	83	0.42	3.4	105	1,350	3.1

(Effect of the Invention)

Since the polyester resin composition of the present invention has excellent moldability in a low-temperature mold while simultaneously having good crystallization characteristics, the generation of gas is low, productivity by means of injection molding and other types of molding is good, the resulting molded article has excellent mechanical properties, and the composition can be used as electrical and electronics components, automotive components, mechanical components, and other parts.

Applicant: Toray Industries, Inc.

² Should probably read (dL/g)